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ENVIRONMENTAL FATE AND EFFECTS OF ORGANOTIN BIOCIDES: A 1/1

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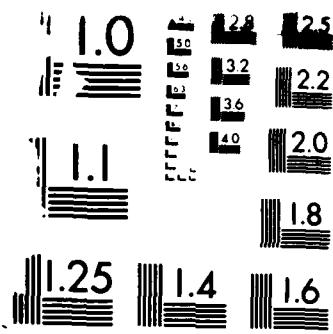
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The goal of this project was to provide a better understanding of the environmental occurrence (marine and estuarine), fate, and effects of the toxic tributyltin species, an active agent in new ship antifouling coatings. We developed ultratrace butyltin measurement methodology, conducted interlaboratory measurement comparisons, and applied the measurement methods to studying the environmental occurrence and fate of butyltin species. We also described a new pathway to environmental methyltin production and provided a new molecular topological correlation of toxicity with total molecular surface area for a number of current and prospective organotin biocides. We collaborated with three Navy laboratories during the course of this research, which resulted in 19 publications and 25 scientific presentations.			
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FINAL REPORT
Environmental Fate and Effects of Organotin Biocides: A
Molecular and Microbiological Assessment

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Introduction

New tributyltin-based antifouling paints, some types already widely used in the private sector, offer significantly improved ship antifouling protection over older copper-based formulations. When we undertook this project with ONR, the U. S. Navy was seeking to implement these antifouling paints incorporating organotin biocides to protect ships hulls and other materials from fouling in marine environments. However, the environmental occurrence, fate and effects of the highly toxic tributyltin species leached from the paints was virtually unexplored.

The goal of this project was to provide the Navy with basic information on the environmental occurrence, fate and effects of tributyltin species to provide the basis for rational decisions on materials design, performance and implementation; monitoring needs and strategies, and assist ongoing modeling efforts. Specifically, we 1) developed advanced measurement methods for detection of tributyltin species and its potential degradation and redistribution products at ambient ultratrace levels in seawater; 2) conducted interlaboratory measurement comparisons to assess international capacities for trace butyltin measurement by alternate means; 3) applied these NBS-developed methods to study the environmental occurrence and pathways of biodegradation of tributyltin species; and 4) provided novel molecular topological correlations between molecular geometry and toxicity of organotin-compounds to provide new insights into candidate second generation organotin

biocide designs. In addition, we conducted experiments on alternate, heretofore unknown potential pathways of environmental organotin biosynthesis and transformations.

Development of Methods for Organotin Chemical Speciation

When we began this research project with ONR in 1983, data on tributyltin occurrence and fate in the marine environment was extremely limited due to the lack of suitable analytical methods for butyltin speciation at environmental sub-ppb levels, particularly in saline media. Consequently, we sought to develop a relatively simple and rapid method for the speciation of tributyltin and its degradation or redistribution products at ng/L (parts-per-trillion) levels in seawater (7,15,17). This method has now been adopted by a number of university, state, and government laboratories in this country and is the method of choice for butyltin analysis by the Department of the Environment in Great Britain and Japan. We provided training and requested demonstration equipment in the use of this method to Navy personnel (DTNSRDC) who are using it for environmental monitoring and paint leaching studies.

The unique method involves the simultaneous extraction and hydridization of organotin species in seawater using dichloromethane and sodium borohydride. The extract, following appropriate preconcentration by evaporation, is analyzed by gas chromatography coupled with tin-selective flame photometric detection (GC-FPD) (Figure 1). The complete group of butyl- and mixed methylbutyltin species is separated and detected at picomolar levels by the technique. Using this methodology, we detected butyltin species in Chesapeake Bay and elsewhere, and reported for the first time the occurrence of tetrabutyltin in natural waters. This compound may be present as an original impurity in tributyltin antifouling paints, or it may arise from chemically or

biologically induced redistribution reactions involving tributyltin. This potential pathway in the environmental fate of tributyltin has not previously been considered although Guard and coworkers at NBL earlier suggested an analogous pathway for trimethyltin reaction in marine sediments.

In addition to the GC-FPD method, we developed a method for measuring total organotins in seawater by graphite furnace atomic absorption spectroscopy (GFAAS). This method featured toluene extraction, deionized water washing of the extract to remove interfering salts, and signal enhancement using an ammonium dichromate matrix modifier (5). This method overcomes frequently reported problems associated with GFAAS for determination of organotins in seawater; especially those associated with sea salt interferences and tin volatilization prior to the atomization procedure. This method complements the GC-FPD procedure by providing rapid, sensitive determination of solvent extractable tin for applications in environmental analysis and controlled release studies using organotin-containing antifouling coatings. Indeed, this NBS method is specified in the current draft proposal method by ASTM Committee D-1, subcommittee D1.45.08, for conducting tests to determine release rates of organotins from organotin-containing antifouling coatings and materials.

We also developed unique methods for tin determination in solution and on surfaces including bacterial cell surfaces, using 3-hydroxyflavone, a fluorescent ligand that is specific for tin(IV) species (11,13). We developed flow injection HPLC coupled with an epifluorescence microscope (EMI) equipped with an emission monochromator-photometer-system for quantitative analysis of inorganic Sn(IV) and certain organotin species at picogram levels in quartz capillary columns under the microscope. The tin-flavonol complex fluoresced

at 460 nm when excited at 365 nm. In addition to detection of tin(IV) in solution, we used flavonol to detect tin on live bacteria that accumulated tin from solution. Under the microscope, cells that accumulated tin fluoresced blue ($\lambda_{\text{ex}} = 365 \text{ nm}$, $\lambda_{\text{em}} = 460 \text{ nm}$) when stained with flavonol. Control cells that accumulated tin and were not stained or that were not exposed to tin and were stained did not fluoresce at the wavelength characteristic of the tin-flavonol complex (460 nm). Non-living particles (glass beads) containing tin(IV) chemically bound to surface mercapto-groups also fluoresced at 460 nm with flavonol (Figure 2), indicating a likely source for key future reference standards.

Interlaboratory Measurement Comparisons

In order to provide Navy and its contractors, as well as regulators, a sound basis for comparison of organotin measurement data, we conducted measurement intercomparisons on environmental samples with Navy laboratories and with research and industrial laboratories worldwide using a NBS-generated tributyltin research material (16).

The research material was generated chromatographically to give an aqueous solution of pure tributyltin hydroxide containing 1.1 mg Sn/L as independently determined by neutron activation analysis (NAA). The material was completely stable when stored in the dark, showing no measurable degradation to di- or monobutyltin species during the year following production. Bottles of the research material were shipped to nearly 50 laboratories in 9 nations. Thirty-five sets of results from thirty-two laboratories were returned to NBS. Participants in the measurement intercomparison measured tin concentrations by their method of choice. The majority of participants (20 to 35) reported tin values close to those of the benchmark NAA value (Figure 3). However, some participants also undertaking

requested chemical speciation of organotin in the sample reported the presence of both di- and monobutyltin species in the research material. We sacrificed a significant quantity (about 10%) of samples to speciate the tin but detected no tributyltin degradation products in any of the samples. The discrepancies between methods strongly suggest that some analytical methods employed induce degradation and/or redistribution of the tributyltin and verify the utility of rigorous interlaboratory comparisons now and in future studies.

We have also conducted a unique measurement intercomparison with the Naval Ocean Systems Center on 14 shared, split samples containing natural levels of butyltin species collected from east and west coasts of the U.S. and from England (10). The analytical agreement between two disparate methods in different laboratories was surprisingly good (Figure 4). In only 5 of 14 samples did our respective results vary by more than 20% of the determined mean concentration for ultratrace tributyltin. We also found that water samples could be stored frozen in polycarbonate containers for up to 2-3 months without serious loss of tributyltin species from the sample, a highly valuable result for organizing all future monitoring studies from diverse locales.

These measurement intercomparisons are of great value to the Navy, EPA and other state and federal agencies that must organize and conduct organotin environmental monitoring programs and consequently will be faced with specifying acceptable methods and qualifications for measurements.

Biodegradation of Tributyltin

We have also provided research results on the pathways and rates of tributyltin degradation in water samples from Chesapeake Bay (9). Although tributyltin-resistant bacteria were isolated from Chesapeake Bay waters, these organisms did not degrade tributyltin in pure cultures in the laboratory.

Thus, the mechanism of resistance to tributyltin does not entail degradation of the organometal, as it does with certain organomercury species where carbon-metal bond cleavage occurs. We did find, however, that substantial degradation of tributyltin to mono- and dibutyltin species occurred in samples of Chesapeake Bay water spiked with tributyltin at 0.1 mg/L (0.1 ppm) and yeast extract (0.05% final concentration). Furthermore, as our measurement methods achieved ng/L (parts-per-trillion) detection limits, we were able to demonstrate the biodegradation of tributyltin spiked into seawater at environmentally realistic (ug/L) levels.

These experiments showed a strong seasonal trend in tributyltin degradation, with rapid degradation (half-lives of 1-2 weeks) of tributyltin occurring in samples collected in summer (Figure 5), and no degradation in wintertime samples incubated at in situ temperatures. Light-stimulated biodegradation suggested the involvement of phytoplankton in tributyltin degradation and we made the novel observation of production of tetrabutyltin in some of these samples. These data (9) along with just published independent results from NOSC, have significantly altered the perception of tributyltin longevity used by modeling programs to predict tributyltin persistence. It is now apparent that rapid tributyltin biodegradation may occur under favorable conditions.

Molecular Topology

Collaborative work with the Naval Biosciences Laboratory led to the discovery that molecular surface areas of 8 triorganotin and 7 diorganotin compounds employed in world-wide commerce, calculated by computer analysis, can be used to accurately predict toxicity to crab larvae (Figure 6) (1,4). Correlation of total surface areas with toxicity is as good as with other established structure-activity predictors (e.g., solubility, Hansch's π

parameter). These findings suggest that for triorganotins, the free energy of aqueous solvation governs their uptake and biological action and can be quite independently estimated from basic bonding (distances, angles, Van der Waal radii) and conformer geometries employing refined holistic TSA calculations (19). Such topological methods, as evidenced by Table 1 (11), should find widespread use in predicting and molecularly tailoring biological activity within a structurally similar series of hydrophobic compounds including candidate second generation Navy organotin biocides.

Exocellular Metabolites Mediating Transformations of Tin and Other Heavy Elements

Finally, we have demonstrated a novel pathway to environmental methyltin formation by the reaction of methyl iodide with SnS (2,3). Methyl iodide is produced globally in large quantities by marine algae and fungi. With SnS, oxidative methylation of tin occurs to produce $\text{CH}_3\text{Sn(IV)}$ species for which strong evidence of a $\text{S}_{\text{N}}2$ mechanism and rapid reaction rates imply importance for tin environmental cycling. In fact, the reaction is so rapid at elevated (60°C) temperatures that it represents a useful new synthesis (yield 33%) for bulk CH_3SnI_3 production. Such methylation pathways may be important in generation of mixed methylbutyltin species we and others found in the environment.

Although very little is known definitely about the biological or chemical pathways to CH_3I generation in nature, it is thought that the metabolite dimethyl-3-propiothetin (DMPT), an intermediate in methionine biosynthesis, might play a role in methyl halide biogenesis. Indeed, we have shown that CH_3I was produced from aqueous mixtures of KI and DMPT (6). Furthermore, we presented evidence that DMPT occurs in Chesapeake Bay phytoplankton. Thus, a previously undescribed route of metal and metalloid methylation in the

estuarine environment may involve methyl halide biogenesis. A summary model for such a process is shown in Figure 7.

Project Outputs

Nineteen refereed archival publications and 25 invited or contributed presentations at scientific meetings resulted from the research conducted on this project.

Acknowledgments

We thank the following collaborators for their contribution to the project: C. L. Matthias (NBS Guest Worker); G. Eng (Institute for Materials Science and Engineering Faculty Appointee); J. S. Thayer (NBS Guest Worker); and E. L. Tierney (NBS Guest Worker).

Table 1

TOPOLOGICAL PREDICTORS FOR ORGANOTIN
PHYSICO-CHEMICAL AND TOXICITY PROPERTIES

Property: Organotins	Measured Value	m(obsd) constant		N	r^2
<u>Aqueous solubility:</u> R_4M (R =alkyl, M =C, Si, Ge, Sn)	-log S molal	0.0224	0.442	9	0.992
<u>Partition coefficient:</u> R_4Sn , octanol/water	log P Σn	0.0263	-1.98	12	0.991
<u>Liquid chromatographic retention:</u> R_4Sn , HPLC	ln κ' min	0.0117	-1.94	12	0.995
<u>Gas chromatographic retention:</u> R_4Sn (R =alkyl, vinyl)	RI min	0.0525	3.64	7	0.983
<u>Microbial uptake:</u> R_3SnCl (R =Et, Pr, Bu)	% uptake Δg	0.459	-69.4	3	0.944
<u>Algal reproduction (growth):</u> R_3SnX-H_2O (R =alkyl, Ph, X =Cl, Br, CO ₃)	ln IC ₅₀ Sn, mg/L	-0.0365	7.69	5	0.957
<u>Larval survival (toxicity):</u> $R_3SnCl-H_2O$ (R =alkyl, Ph, c-Hx)	ln LD ₅₀ nM	-0.0146	9.18	8	0.938

$$\ln [\text{PROPERTY}] = m \times [\text{TSA}] + \text{constant}$$

Figure Captions

Figure 1. Chromatogram showing separation of butyltin species (4-5 ng each) by the GC-FPD method.

Figure 2. Microspectrofluorograms of cells and glass beads exposed to combinations of SnCl_4 and flavonol. The emission spectrum of flavonol alone is shown in top figure. Excitation wavelength was 365 nm.

Figure 3. Frequency diagram of the results of analysis of the tributyltin research material by intercomparison participants. The total number of participants was 32. The analytical methods used (coded A to G) are located above a concentration scale indicating the distribution of values determined. The results tend to be evenly distributed about the center (1.0 ppm) point.

Figure 4. Graph of HD-AA (NOSC) values versus GC-FPD (NBS) values for tributyltin species from environmental seawater samples. The plotted line has a slope of 1.0, that of theoretically perfect agreement between the two methods.

Figure 5. Time course of butyltin speciation with summertime water temperature conditions. Chesapeake Bay water collected in early September, spiked with tributyltin and incubated at 28°C under 40-W incandescent lamps, or in the dark. Tetrabutyltin occurred sporadically in some of these samples but is not shown in the figure. Concentrations shown are means of duplicate samples.

Figure 6. Correlation between calculated TSA values for all major commercial organotins and their experimentally determined LC50 concentrations for crab larvae for di- and triorganotin compounds.

Figure 7. Model proposed for either endo- or exo-cellular methylation of metals and metalloids involves initial production of methyl iodide via reaction between DMPT and membrane-permeable iodide followed either by intra- or extra-cellular transfer of methyl carbonium ion to a nucleophilic center. Shown is exocellular methylation of stannous ion following excretion of precursor MeI from the cell. Direct methylation of a nucleophile by the DMPT metabolite is possible but not yet demonstrated. Removal of "active" methyl by environmental sulfur compounds and -OH probably strongly competes with metal(loid) methylations.

Fig. 1

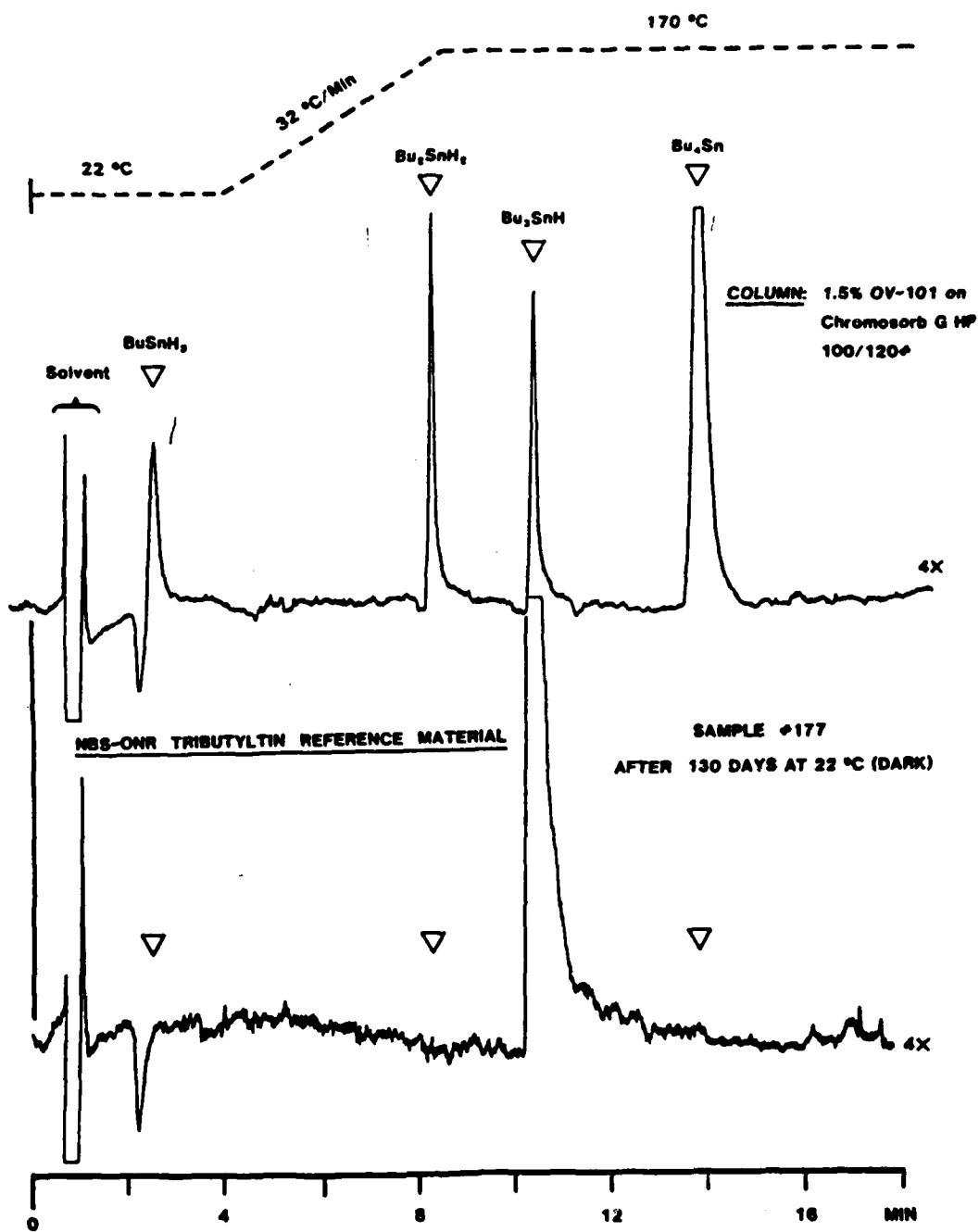


Fig. 2

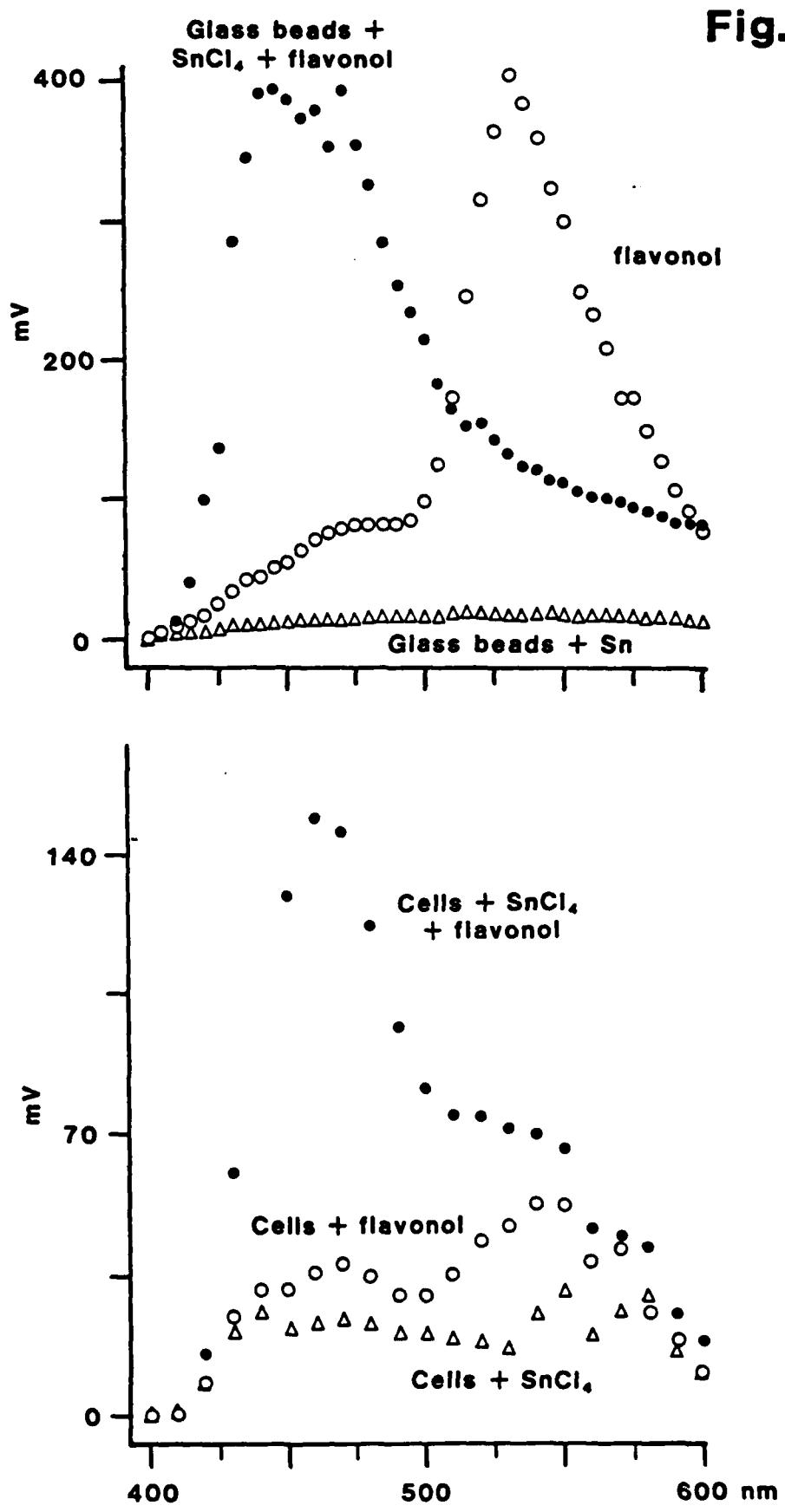


Fig. 3

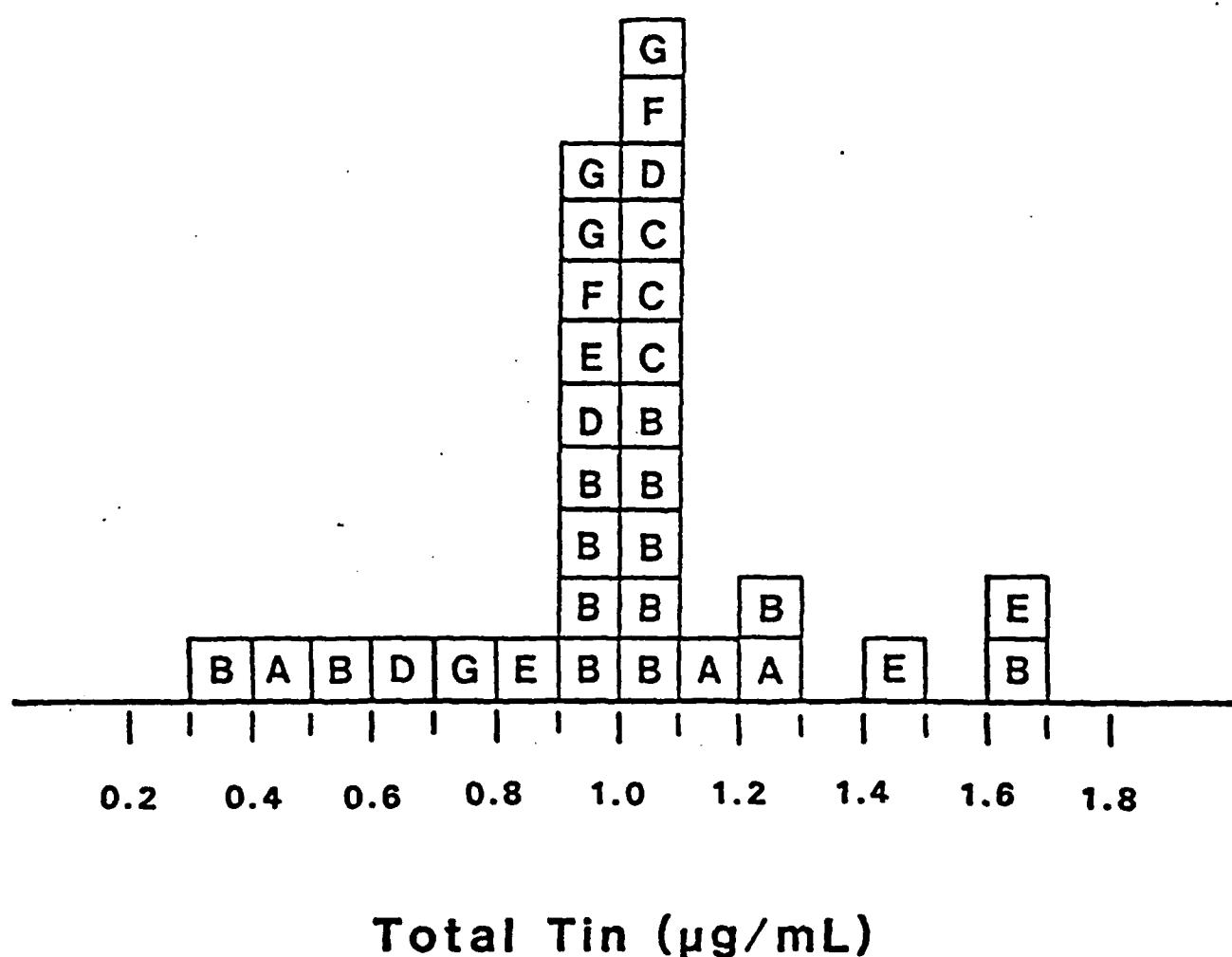


Fig. 4

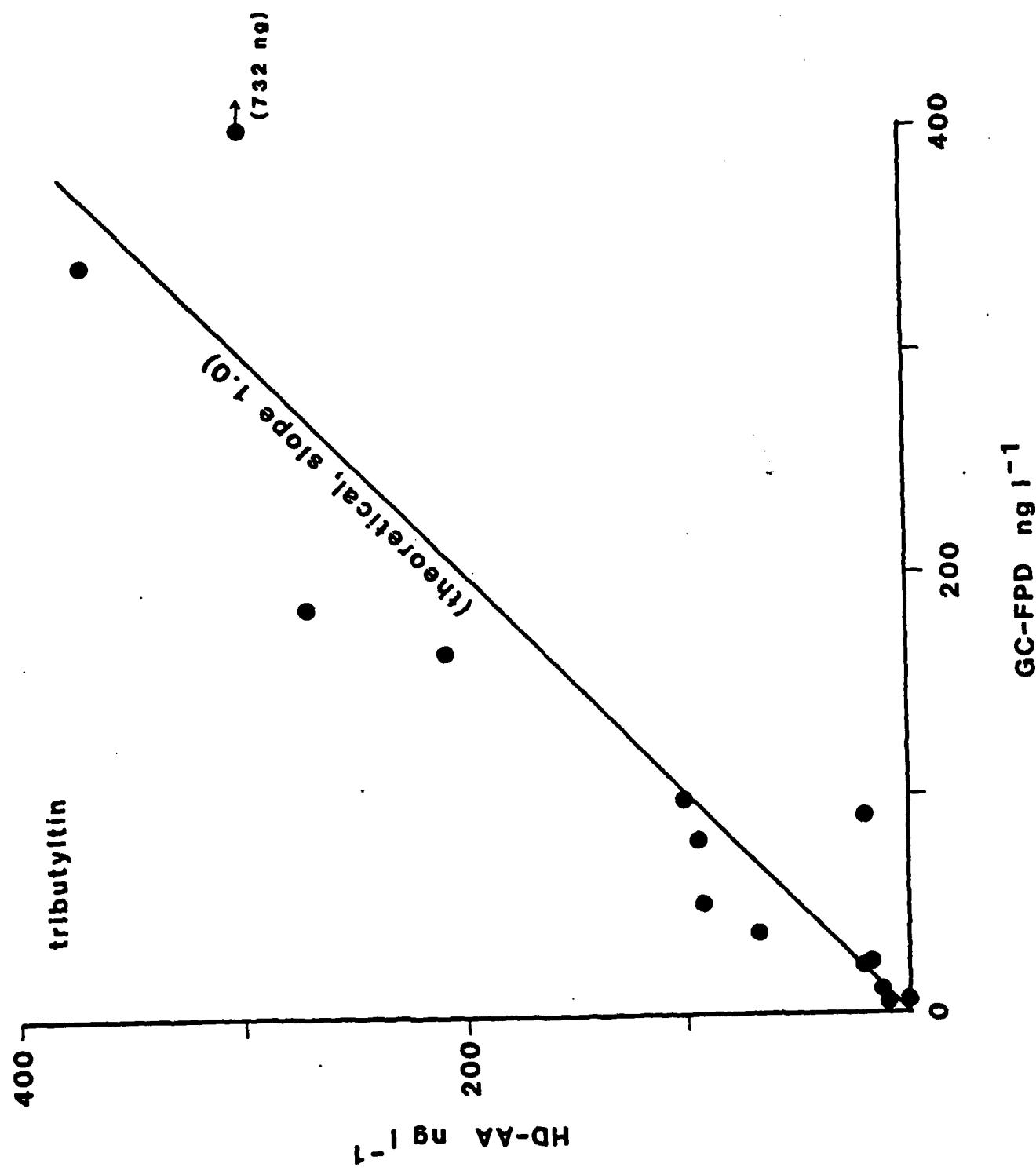
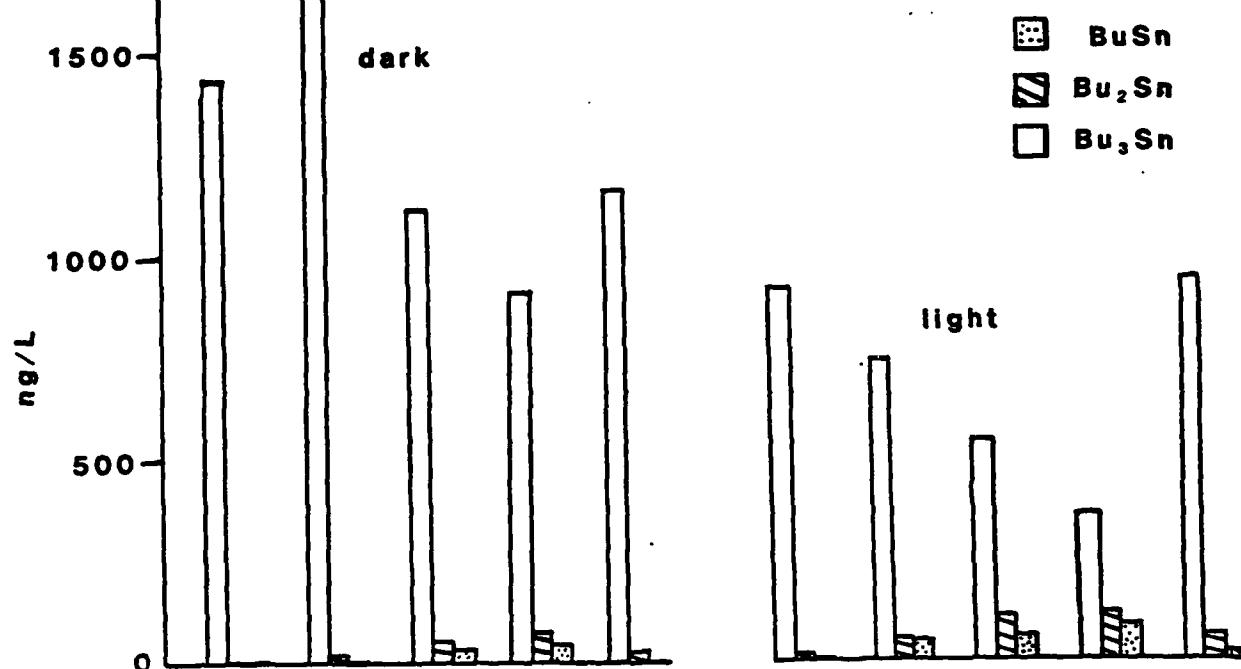


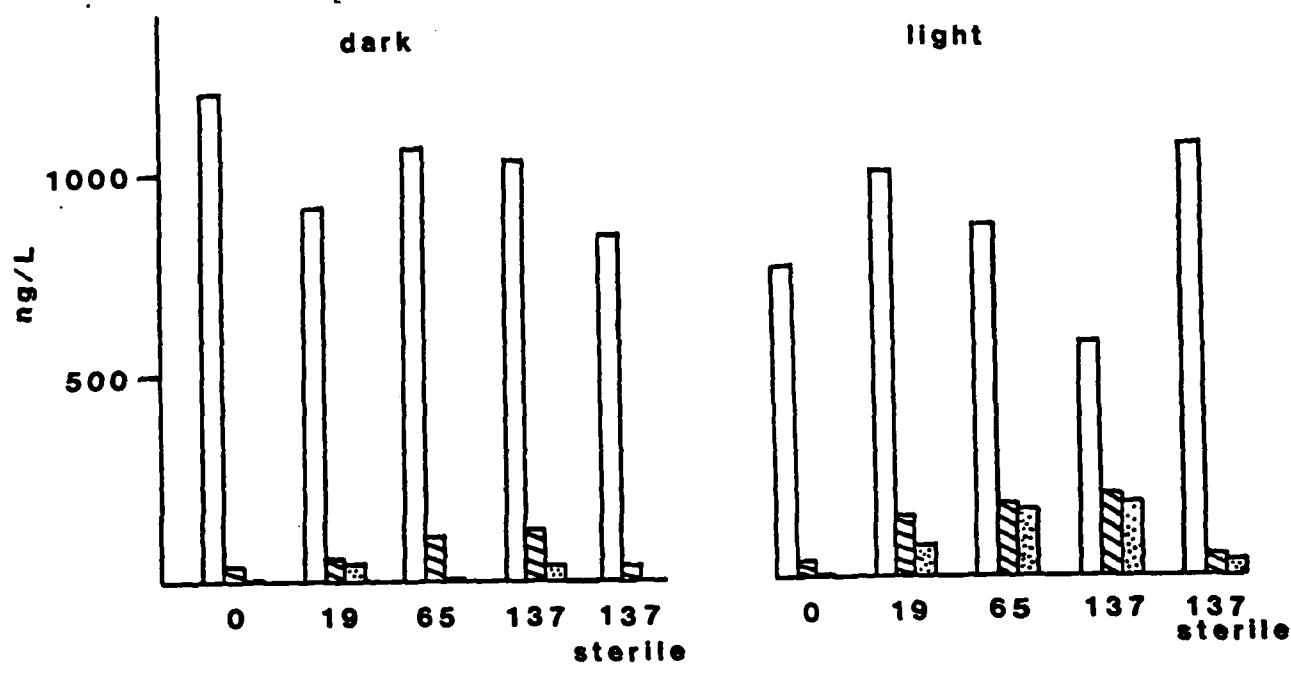
Fig. 5

September 28 °C

BALTIMORE HARBOR



ANNAPOLIS



HOURS

Fig 6

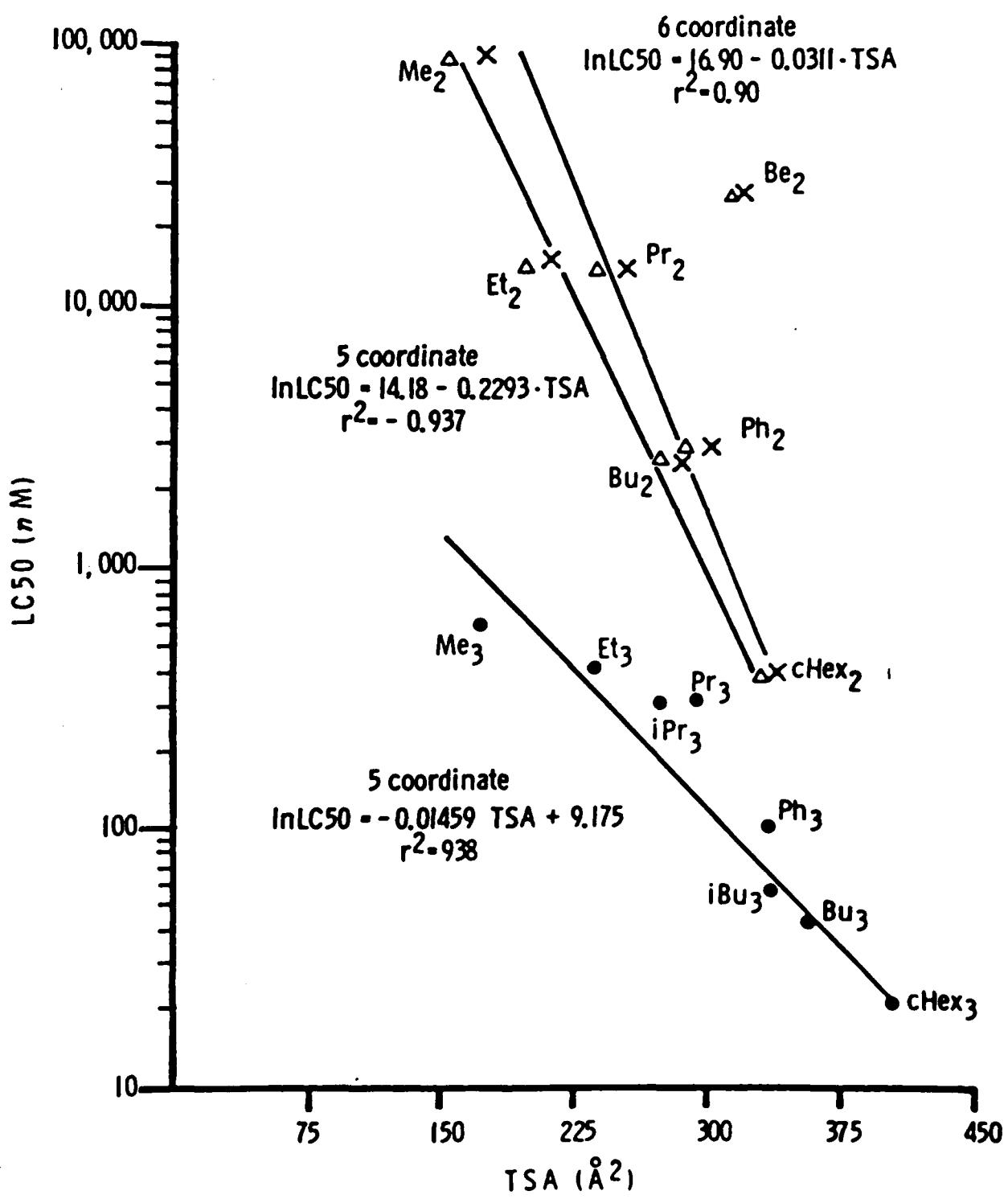
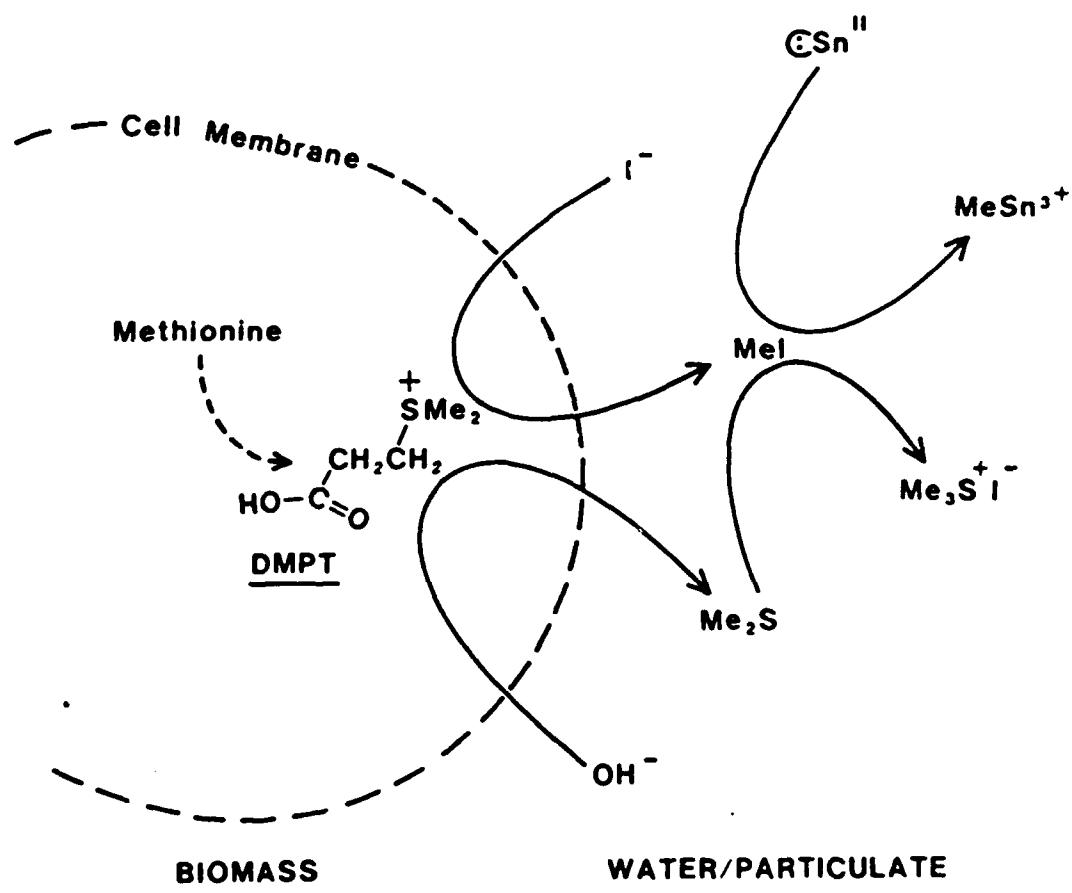


Fig. 7



Environmental Fate and Effect of Organotin Biocides: A Molecular and Microbiological Assessment

Project Publications:

1. "Predictive Toxicity Using Computed Molecular Topologies: The Example of Trioorganotin Compounds," R. B. Laughlin, W. French, R. B. Johannesen, H. E. Guard, and F. E. Brinckman, *Chemosphere* 13, 575-584 (1984).
2. "A Novel Synthesis of Methyltin Triiodide with Environmental Implications," W. F. Manders, G. J. Olson, F. E. Brinckman, and J. M. Bellama, *J. Chem. Soc. Chem. Comm.* 538-540 (1984).
3. "Iodomethane as a Potential Metal Mobilizing Agent in Nature," J. S. Thayer, G. J. Olson, and F. E. Brinckman, *Environ. Sci. Technol.* 18, 726-729 (1984).
4. "Structure-Activity Relationships for Organotin Compounds," R. B. Laughlin, R. B. Johannesen, W. French, H. E. Guard, and F. E. Brinckman, *Environ. Toxicol. Chem.* 4, 343-351 (1985).
5. "GFAAS Determination of Ultra-trace Quantities of Organotins in Sea Water by Using Enhancement Methods," E. J. Parks, W. R. Blair, and F. E. Brinckman, *Talanta* 32, 633-639 (1985).
6. "Biological Mediation of Marine Metal Cycles: The Case of Methyl Iodide," F. E. Brinckman, G. J. Olson, and J. S. Thayer, in: Marine and Estuarine Geochemistry. A. Sigleo and A. Hattori, Eds., Lewis Publ., Chelsea, MI, (1985) pp. 227-238.
7. "A Comprehensive Method for the Determination of Aquatic Butyltin and Butylmethylin Species at Ultra-trace Levels Using Simultaneous Hydridization/Extraction with GC-FPD," C. Matthias, J. M. Bellama, G. J. Olson, and F. E. Brinckman, *Environ. Sci. Technol.* 20, 609-615 (1986).
8. "The Molecular Nature of Tin in Cellular Media: An Abstract," F. E. Brinckman, in: Tin as a Vital Nutrient: Implications in Cancer Prophylaxis and Other Physiological Processes, N. F. Cardarelli, Ed., CRC Press, Inc., Boca Raton, FL (1986), p. 243.
9. "Biodegradation of Tributyltin by Chesapeake Bay Microorganisms," G. J. Olson and F. E. Brinckman, in: Proc. Oceans '86, Vol. 4, Organotin Symp., Marine Technol. Soc., Washington, D. C. (1986), pp. 1196-1201.
10. "Di- and Tributyltin Species in Marine and Estuarine Waters: Interlaboratory Comparison of Two Ultratrace Analytical Methods Employing Hydridization and Atomic Absorption or Flame Photometric Detection," A. O. Valkirs, P. F. Seligman, G. J. Olson, F. E. Brinckman, C. L. Matthias, and J. M. Bellama, *The Analyst*, (1986) in press.

11. "Implications of Molecular Speciation and Topology of Environmental Metals: Uptake and Toxicity of Organotins," F. E. Brinckman, G. J. Olson, W. R. Blair, and E. J. Parks, in: Proc. Tenth Symp. Aquatic Toxicol. and Hazard Assessment, ASTM Publ., Philadelphia, PA, in press.
12. "Methods for the Analysis of Organometallic Compounds in Wastes," G. J. Olson, F. E. Brinckman, and W. R. Blair, in: Proc. 2nd Annual EPA Symp. Solid Waste Testing and Quality Assurance, in press.
13. "Characterization of Organotin Species Using Microbore and Capillary Liquid Chromatographic Techniques with an Epifluorescence Microscope as a Novel Imaging Detector," W. R. Blair, E. J. Parks, G. J. Olson, F. E. Brinckman, M. C. Valeiras-Price, and J. M. Bellama, in preparation.
14. "Speciation Measurements of Butyltins: Applications to Controlled Release Rate Determination and Production of Reference Standards," W. R. Blair, G. J. Olson, and F. E. Brinckman, in: Proc. Oceans '86 Conf., Vol. 4, Organotin Symp., Marine Technol. Soc., Washington, D.C. (1986) pp. 1141-1145.
15. "A Comprehensive Method for the Determination of Aquatic Butyltin Species at Ultratrace Levels Using Simultaneous Hydridization/Extraction with GC-FPD," G. J. Olson, F. E. Brinckman, C. L. Matthias, and J. M. Bellama, NBSIR 85-3295 (prepared for Naval Ship Research and Development Center), December, 1985, 48 pp.
16. "An International Butyltin Measurement Methods Intercomparison: Sample Preparation and Results of Analyses," W. R. Blair, G. J. Olson, F. E. Brinckman, R. C. Paule, and D. A. Becker, NBSIR 86-3321 (prepared for the Office of Naval Research), February, 1986, 56 pp.
17. "Determination of Ultratrace Concentrations of Butyltin Compounds in Water by Simultaneous Hydridization/Extraction with GC-FPD Detection," C. L. Matthias, J. M. Bellama, and F. E. Brinckman, in: Proc. Oceans '86 Conf., Vol. 4, Organotin Symp., Marine Technol. Soc., Washington, D.C. (1986), pp. 1146-1151.
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19. "Holistic Conformational and Total Surface Area Calculations as Predictors for Solution Properties and Chromatographic Parameters: Organometals," G. Eng, F. E. Brinckman, R. B. Johannessen, L. Tierney, and J. M. Bellama," in preparation.

Project Presentations:

1. "Speciation and Molecular Topology as Predictors of Microbial Uptake of Metals," F. E. Brinckman, Gordon Research Conference on Microbiological Degradation, Brewster Academy, Wolfsboro, NH, July 1983.
2. "Environmental Effects of Organotins," F. E. Brinckman, Fourth International Conf. on the Organometallic and Coordination Chemistry of Germanium, Tin, and Lead, McGill University, Montreal, Quebec, Canada, August 1983.
3. "Molecular Properties of Tin- and Lead-Bearing Macromolecules: Poly(triorganotin)methacrylate and a Copolymer of 4-vinylphenyltriphenyl lead and Octadecylmethacrylate," E. J. Parks and F. E. Brinckman, XI International Conf. on Organometallic Chemistry, Pine Mountain, GA, September 1983.
4. "The Release of Metals from Sediments by Iodomethane," J. S. Thayer, T. W. Brueggemeyer, G. J. Olson, and F. E. Brinckman, 186th National Meeting, Am. Chem. Soc., Div. Environ. Chem., Washington, D.C., September 1983.
5. "Simultaneous Speciation of Tin and Mercury in Water Using a Gas Chromatograph with Flame Photometric and Atomic Absorption Detection," G. J. Olson and F. E. Brinckman, 186th National Meeting, Am. Chem. Soc., Div. Anal. Chem., Washington, D.C., September 1983.
6. "Solubilization of Sedimentary Metals by Aqueous Methyl Iodide," Sixth International Symposium on Environmental Biogeochemistry, G. J. Olson, F. E. Brinckman, and J. S. Thayer, Santa Fe, NM, October 1983 (poster).
7. "Structure-Activity Relationships for Organotin Compounds," E. J. Parks, W. R. Blair, G. J. Olson and F. E. Brinckman, Fourth Annual Meeting of the Society of Environmental Toxicology and Chemistry, Arlington, VA, November 1983 (presented by R. B. Laughlin).
8. "Chemical and Biological Extraction for Chromatographic Speciation of Tributyltin for Assessment of Environmental Fate and Impact," E. J. Parks, W. R. Blair, G. J. Olson and F. E. Brinckman, 8th International Symp. on Column Liquid Chromatography, New York, NY, May 1984.
9. "HPLC-Atomic Absorption Spectroscopy for Trace Metal Analysis and Speciation," F. E. Brinckman, Ninth Annual Spring Training Workshop, Assn. Official Analytical Chemists, Philadelphia, PA, May 1984.
10. "The Molecular Nature of Tin in Cellular Media," F. E. Brinckman, International Symposium on Effect of Tin Upon Malignant Cell Growth, Univ. of Scranton, Scranton, PA, May 1984.

11. "Molecular Speciation of Environmental Metals," F. E. Brinckman, Dept. of Environmental Health Sciences, School of Hygiene and Public Health, Johns Hopkins University, Baltimore, MD, May 1984.
12. "Epifluorescence Microscope Detector Coupled with Microbore HPLC for Speciation of Bioactive Organotins at Sub-Picomolar Levels," F. E. Brinckman, G. J. Olson, W. R. Blair, and E. J. Parks, 188th National Meeting, Am. Chem. Soc., Div. Anal. Chem., Philadelphia, PA, August 1984.
13. "Biological Mediation of Marine Metal Cycles: The Case of Methyl Iodide," F. E. Brinckman, G. J. Olson, and J. S. Thayer, International Chemical Congress, Pacific Basin Societies, Honolulu, HI, December 1984.
14. "Speciation and Molecular Topology as Predictors of Microbial Uptake of Metals," F. E. Brinckman, Am. Soc. Microbiol. Annual Meeting, Las Vegas, NV, March 1985.
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